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INVESTIGATION OF EFFECTS OF ION-INDUCED DEFECTS ON SURFACE REACTIONS

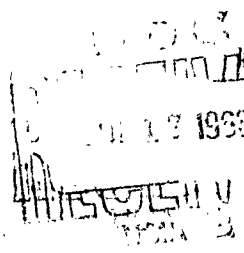
Final Report
20 January 1961 - 19 January 1963

Contract No. AF 19(604)-8004

Y. Margoninski
D. Shooter

Project 5620
Task 562003

RAYTHEON COMPANY
Research Division
Waltham 54, Massachusetts



Prepared for

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS

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FOREWORD

This Final Report is written in three separate series, corresponding to the three major projects specified in the work statement of the contract:

Project A: Sputtering and Adsorption Properties of the (111) Faces of Gallium Antimonide

Project B: A Survey of the Electrical Measurements Suited for Studying the Effects of Adsorbed Species on Surface Phenomena

Project C: Simultaneous Measurements of Filament Lifetime and Surface Conductivity on Clean and Oxidized Germanium Surfaces.

Section 1 of this report was written by D. Shooter, Sections 2 and 3 by Y. Margoninski. From January 1961 to June 1961 S. P. Wolsky supervised Project A, and after that date D. Shooter took over this Project until its termination in November 1962. Project C, supervised by Y. Margoninski, was terminated in April 1963.

Section 1. Project A. Sputtering and Adsorption Properties of the (111)
Faces of Gallium Antimonide

The earlier phases of this work have been fully described in the following scientific reports:

- No. 1: AFCRL 381; S-285, "The Characteristics and Application of a Simple Quartz Microbalance," by S. P. Wolsky and E. J. Zdanuk.*
- No. 2: AFCRL-62-935; S-472, "The Sputtering of Compounds," by S. P. Wolsky, E. J. Zdanuk, and D. Shooter.**
- No. 3: AFCRL-62-924; S-480: "The Adsorption of Oxygen on Gallium Antimonide," by D. Shooter.***

Further work done in the latter part of the contract interval is described below.

High Pressure Experiments

The experiments at low oxygen pressures have shown that a clean gallium antimonide surface adsorbs oxygen for a certain period of time and then the adsorption ceases. If the pressure is increased to one Torr there is a further uptake but this also ceases in about 100 minutes. The adsorption is not an indefinite logarithmic uptake as has been observed for crushed samples.¹ A number of experiments have been made by admitting oxygen at high pressure to a clean sample. The results are given in Table I together with two low pressure experiments for comparison. This shows that the rates of adsorption and amounts of oxygen adsorbed are less reproducible than in the low pressure experiments, even though contamination

*Published in Vacuum Microbalance Techniques, Vol. 2., Plenum Press, N. Y. (1962), p. 37

**Presented at the 9th Annual Symposium of the American Vacuum Society, Los Angeles (1962).

***Presented at the 3rd Symposium on Vacuum Microbalance Techniques, Los Angeles (1962).

TABLE I
ADSORPTION OF OXYGEN ON GaSb AT HIGH PRESSURES

<u>Face Exposed</u>		<u>K_e ($\times 10^3 \text{ min}^{-1}$)</u>	<u>Pressure (torr)</u>	<u>Molecules Adsorbed ($\times 10^{-16}$)</u>
(111)	Ga	36.7	0.5	2.8
	Ga	13.8	0.5	2.5
	Ga	30.9	0.5	2.2
$(\bar{1}\bar{1}\bar{1})$	Sb	26.6	0.4	2.3
	Sb	24.4	0.8	1.4
	Sb	39.4	0.8	1.6
---		---	---	---
(111)	Ga	74.8	2×10^{-6}	1.1
$(\bar{1}\bar{1}\bar{1})$	Sb	51.6	3.6×10^{-6}	2.0

was no more likely. No correspondence exists between the amount adsorbed and the rate of adsorption. It is also interesting that in two runs made on the $(\bar{1}\bar{1}\bar{1})$ or antimony face the amount adsorbed was less than that observed in low pressure experiments. The data can be expressed by a similar equation $\ln(1-W/W_\infty) = K_e t$, but the velocity constants K_e are actually lower than examples given in Table I for the low pressure experiments in spite of a 10^6 increase in pressure. K_e does not appear to depend on pressure in this range. If contamination is ruled out, then it is obvious that a different process is rate controlling in the higher pressure range. This process is more sensitive to the surface condition than the low pressure reaction. Wolsky² has reported a similar lack of reproducibility using the same apparatus and experimental conditions for the oxidation of germanium.

Annealed Surface

After three experiments on the (111) face it became necessary to open the system and rebalance the microbalance so the opportunity was

taken to reverse the samples and expose the $(\bar{1}\bar{1}\bar{1})$ faces. When three runs on these faces gave a similar lack of reproducibility an attempt was made to anneal the sample surface. The experimental procedure was : the sample was heated by a furnace outside the experimental tube to a temperature of 400 °C (also measured externally.) It was then bombarded with 500 ev ions, allowed to remain at the high temperature for 15 minutes, and then gradually cooled to room temperature. Oxygen at low pressure was then admitted to the sample, with the result shown in Fig. 1 for two consecutive experiments. The sample first increased in weight then decreased becoming lighter than it was at the beginning of the experiment. These weight changes were observed for oxygen only on a cleaned surface.

A decrease in weight might be caused by oxygen displacing a contaminant of heavier molecular weight which is only loosely bound to the surface. CO_2 might be such a contaminant, but a calculation using the known sticking coefficient³ and the observed omegatron scans shows that the pressure in the system is too low by at least two orders of magnitude. The curve is also the wrong shape for a reaction $(\text{GaSb}) - \text{CO}_2 + \text{O}_2 = (\text{GaSb}) - \text{O}_2 + \text{CO}_2$.

Further experiments were then made on unannealed surfaces but the results of the earlier low pressure experiments could not be repeated. At this point the system was opened to the atmosphere and re-evacuated. The first four runs on unannealed surfaces followed the usual equation but were not reproducible in terms of the rate or amount absorbed. In two runs following these, the unannealed surfaces showed a maximum in the adsorption curve similar to that observed for annealed surfaces (Fig. 2). The surface-cleaning treatment was altered by varying the incident ion energy between 400 and 700 ev, and increasing the current density and bombardment time. No improvement in the reproducibility of the adsorption results was obtained.

It appears that heating the crystal has caused a permanent change in the $(\bar{1}\bar{1}\bar{1})$ surface and that normal ion bombardment technique, or even exposure to the atmosphere, does not restore the surface which gave the original reproducible low pressure results. A possible explanation of the weight decrease observed is the evaporation of the volatile oxide Sb_4O_6 from the surface. This has been observed to evaporate from InSb at 200°C^3 and since Sb_4O_6 has such a large molecular weight only a small amount of evaporation would account for the observed weight decrease. The weight loss on heating an oxygen covered $(\bar{1}\bar{1}\bar{1})$ surface is equivalent to a monolayer of Sb_4O_6 .

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3. A. J. Rosenberg, J. Phys. Chem. 64, 1135 (1960).

FIGURE CAPTIONS

<u>Number</u>	<u>Title</u>
1	Adsorption Curves for Annealed ($\bar{1}\bar{1}\bar{1}$) Surfaces
2	Adsorption Curves for Unannealed ($\bar{1}\bar{1}\bar{1}$) Surfaces

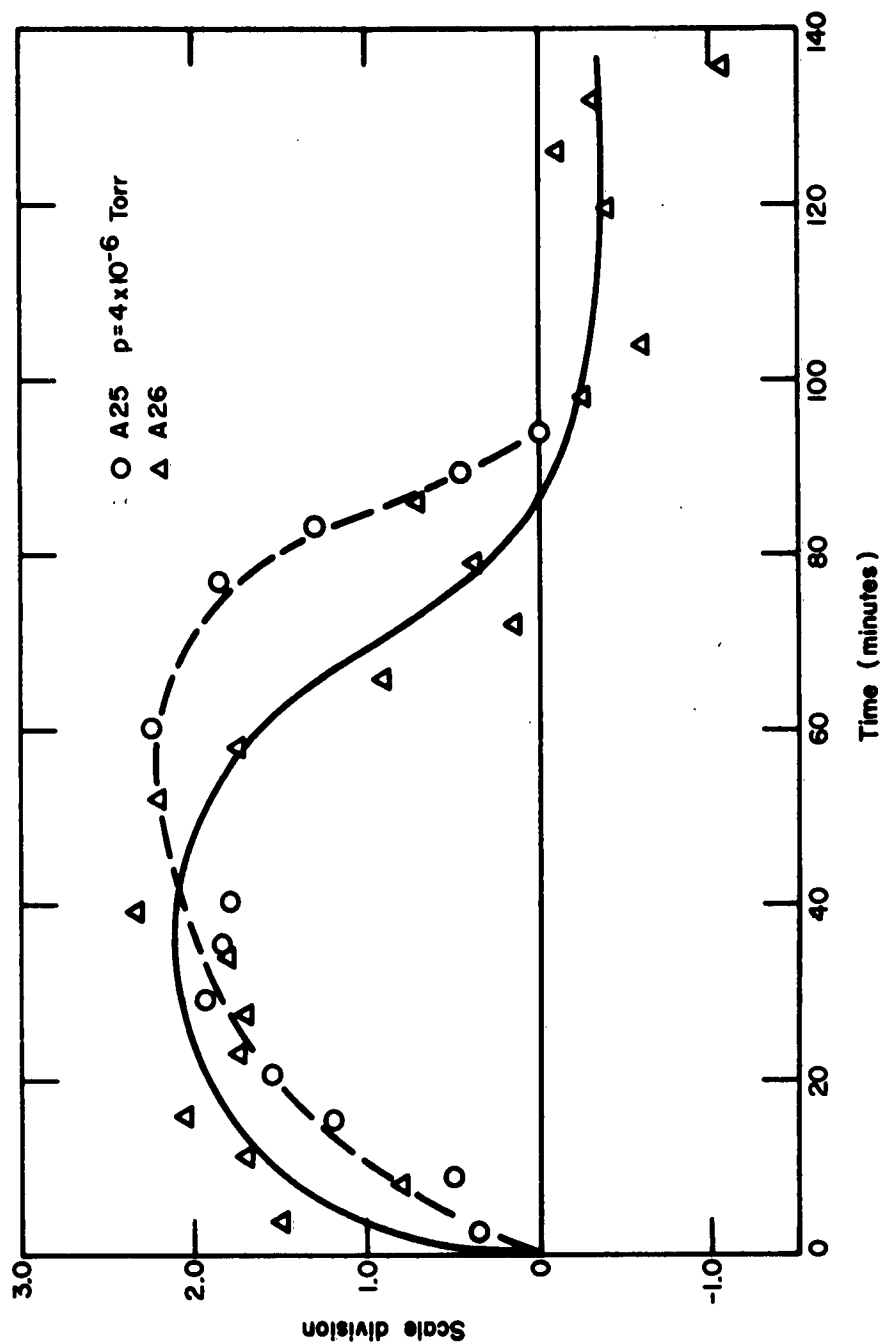


FIGURE 1

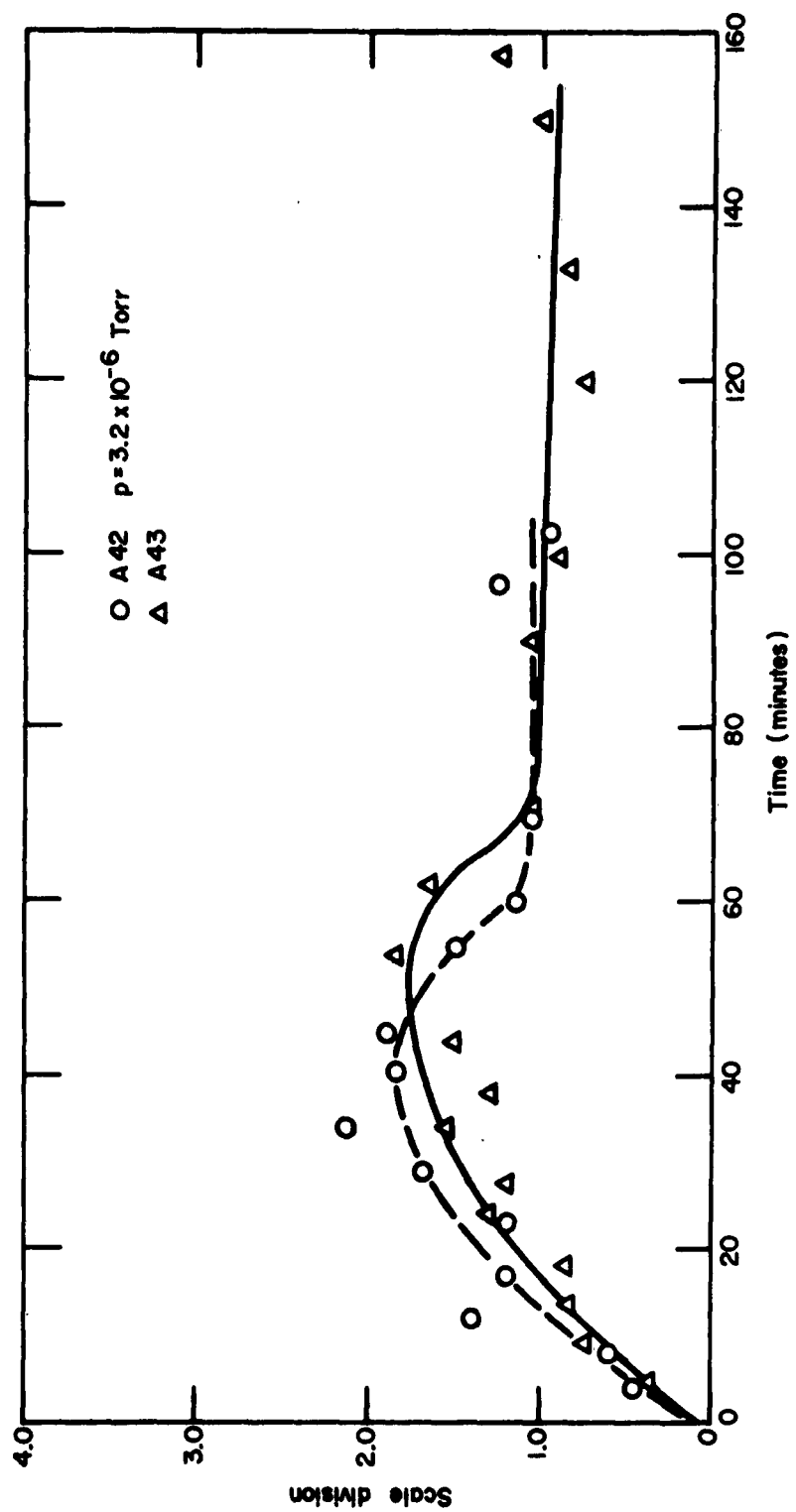


FIGURE 2

Section 2. Project B. A Survey of the Electrical Measurements Suited for Studying the Effects of Adsorbed Species on Surface Phenomena

In this brief survey the following methods will be discussed:

1. Flash filament technique
2. Work function measurements
3. Low energy electron diffraction studies
4. Surface auger effect
5. Field emission microscopy
6. Surface recombination, conductivity, and mobility measurements.

1. Flash Filament Technique

An important parameter in the study of gas adsorption on clean surfaces is the "sticking coefficient," i. e., the ratio of: (particles adsorbed on surface)/(particles striking surface). The easiest way to measure this parameter is by the "flash filament technique"¹: the material to be studied is prepared in ribbon or filament form of known surface area. It is introduced into the gas ambient, at very low pressure. The filament is heated to a high temperature for a sufficient interval to desorb the adsorbed gas from the surface. It is then cooled for a known time and reheated rapidly to a temperature where all the adsorbed gas is desorbed. From the change in pressure in the known volume, the surface area of the filament etc., the sticking coefficient can be readily obtained. From the experimental viewpoint this is a very easy measurement to perform and needs no special equipment. It can also be extended to a mixture of ambients, because each of the constituents will desorb from the filament at a different temperature. Recently Kornelsen² has measured the entrapment and the thermal desorption of inert gases in tungsten by a very elegant application of the flash filament technique.

2. Work Function Measurements

The work function of a metal or semiconductor is extremely sensitive to contamination. It is, therefore, well suited to indicate the "cleanliness" of a given surface and to detect the changes in the energy band structure resulting from different bulk dopings, adsorption of gases etc. Measurements of this kind were first performed by Dillon and Farnsworth,³ who used a combination of the Fowler photoelectric yield method and the Kelvin contact potential method. Allen⁴ measured the dependence of the work function on crystal orientation, using the Kelvin method. The setup for these experiments is complicated and justified only if one has a specific interest in the absolute value of the work function. Relative values of the work function can be detected in a much simpler way by field emission.

3. Low-Energy Electron Diffraction Studies

This is one of the most powerful and versatile methods for the study of clean, unperturbed metal or semiconductor surfaces. Its underlying principle is similar to Bragg's X-ray diffraction technique: a beam of low (10 to 200 ev) energy electrons is directed onto a crystal face and the resulting diffraction pattern studied by a suitable low-current probe (e. g. , a Faraday cage). From the angle and intensity of the diffracted electron beam the lattice constant and the relative density and position of the surface lattice atoms can be obtained. Sticking coefficients can also be measured. Reference 5 is a well-written and authentic survey of this technique. Reference 6 is a good example of the wealth of important and accurate information obtained by it.

The design and construction of an electron diffraction tube is quite difficult, as it involves many moving parts. The alignments between the electron gun, the crystal, and the collector must be accurate. Recently Germer⁷ constructed a tube in which the diffracted electrons are not collected by a probe, but accelerated toward a fluorescent screen. In this

manner the diffraction pattern is observed on a screen, and not measured "point by point." This a faster and less laborious way to obtain the data. This "Post Diffraction Acceleration" (PDA) tube has two disadvantages over the older "collector type" instrument: the observable range of colatitude angle is restricted (unless a cylindrical geometry is used) and the intensity of the diffracted electron beams can only be deduced from the brightness of the diffraction spot on the screen. These two shortcomings are not important, and judging by the number of diffraction tubes that have been constructed recently, the PDA tube is the more popular choice. Low-energy electron diffraction measurements are the most reliable means to test the cleanliness of a given crystal surface. The colatitude angle and the sharpness of the electron beam are directly related to the lattice structure of the surface and thereby yield immediate information on its state: Whether it is atomically clean or covered by a layer of foreign material of known structure (amorphous or crystalline) and thickness (fractions of a monolayer, etc.). There are many ways of obtaining a clean surface: cleavage, heating, ion bombardment and annealing, heating after chemical treatment⁸ etc., but only those are reliable that have been tested previously by electron diffraction measurements. Any study intended to find new ways for obtaining clean surfaces,⁸ or applying known techniques to samples not previously tested (e. g., semiconducting diamond⁹) should most definitely include low-energy electron diffraction measurements.

4. Surface Auger Effect

Slow-moving noble gas ions interacting with a solid surface can cause a process involving the release of two electrons from the filled band. The first electron tunnels from the valence band through to the ground state of the incident ion, thereby neutralizing it. The second electron picks up the excess energy of this process and becomes a fast internal secondary or Auger electron. The experiment consists of measuring the total yield and the kinetic energy distribution of those Auger electrons which leave the solid.¹⁰ Measurements on germanium proved to be sensitive to the adsorption

of a monolayer or less of gases like CO and O₂, but could not differentiate between an annealed and unannealed surface.¹¹ As a diagnostic tool for the study of surfaces this method is much inferior to electron diffraction; its chief value lies in the fact that some information on the density of states in the valence band can be obtained, and this only after a formidable amount of computation.¹⁰

5. Field Emission Microscopy

The field electron emission microscope (FEEM) projects a highly magnified image ($10^6\times$ is a typical value) of a sharply pointed emitting tip onto a fluorescent screen. The electron emission from the tip occurs by tunneling, caused by large applied fields. The image in the FEEM results from variation in work function and local field strength over the surface of the tip. For a single crystal these variations occur with the same symmetry as that of the crystal. Since the emission current depends exponentially on both the work function and the local field strength, changes in either of these two parameters are easily detected. Unfortunately, it is rarely possible to unambiguously separate the electronic effect of change in work function from the structural effect of local field variation. The FEEM is an excellent tool for the study of surfaces. It provides an immediate visual image of the single crystal studied (similar to the PDA tube) and of all the crystallographic faces at once. The image is highly sensitive to any foreign atoms that can alter the work function. Under vacuum conditions of 10^{-10} torr a tip that has been cleaned once will remain so for hours. The specimen can be heated, cooled, field-desorbed, contaminated with atoms of gases or solids, recleaned again and remain under direct observation all the time. Diffusion of foreign atoms from the bulk to the surface as well as surface migration are readily observed. Compared to the electron diffraction tube, the apparatus is very simple: There are no moving parts, no electron guns, no cylindrical shields. But there are some important disadvantages:

1) The sample geometry is limited to very fine tips, and as a result 2) it is impossible to carry out other sensitive electrical measurements on the same surface, 3) the surface is always under the influence of enormous electric fields, which subject it to forces of about one ton per sq cm. It can therefore never be regarded as unperturbed. 4) It is difficult to get precise numerical data on surface properties.

References 12 and 13 are excellent reviews on field emission microscopes, their capabilities and merits compared to other techniques.

6. Surface Recombination, Conductivity, and Mobility Measurements

Measurements of surface recombination and surface conductivity have proved very successful in studying the parameters of the surface states on real germanium and silicon surfaces. Both measurements utilize the field effect, i. e., the surface potential of the sample is varied by a strong electrostatic field. For an oxide covered germanium surface a field of $\pm 10^6$ v/cm causes the surface potential to change by about 12-16 kT, this range is usually sufficient to determine unambiguously the surface state structure in the midgap region. Clean germanium surfaces are strongly p-type or even degenerate, therefore the same electrostatic field will cause a change in surface potential by less than 1kT. Hence these measurements will be less effective and successful on clean surfaces, unless means will be found to apply much stronger fields. These are other ways of changing the surface potential, e. g., adsorption of oxygen or other gases, but these are unreliable because they are known to affect and alter the surface states. Still, some interesting results have been obtained by measuring changes in surface recombination and conductivity as a function of oxygen adsorption, see Ref. 14 and even 15.

Conductivity measurements are relatively easy to perform; to measure surface recombination requires more care and experience. The

experimental setup for field effect measurements on clean surfaces can be quite complicated¹⁵ and the pitfalls are many.^{14, 16} They can therefore only be justified or recommended in the following circumstances:

1. Any knowledge about surface states, even if limited, is of importance. Despite its many disadvantages and limitations¹⁴ this is still the best method for studying surface states, though some information of this nature may also be obtained from field emission, photoelectric threshold and work function,¹⁷ and the surface Auger effect.¹⁸
2. Utmost sensitivity is required. Surface conductance may easily be affected by a coverage of about 0.1 to 1 percent of a monolayer, because this corresponds to a carrier density of 10^{12} to 10^{13} per sq cm. This is about 5 to 50 times more sensitive than electron diffraction measurements.¹⁴

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Section 3. Project C. Simultaneous Measurements of Recombination and Conductivity of Clean and Oxidized Germanium Surfaces

I. INTRODUCTION

"Clean" germanium surfaces were first obtained by Farnsworth¹ and his collaborators in 1955, they were also the first to measure the work function² and to obtain some information on the structure of the surface lattice from their low energy electron diffraction data.³ Since the Semiconductor Surface Conference at Philadelphia in 1956 many more measurements were performed on clean germanium surfaces, chiefly with the intention to obtain information on the surface states, but very few of these compare in reliability and importance with those reported by Farnsworth. (For a review of this field, see Ref. 4). Our knowledge about the surface states is still very meagre and we have no reliable information on their distribution, density, or capture cross section. For "real surfaces" the situation is different and most of the important parameters of the surface states are well known. The main reason for the lack of reliable information on clean surfaces is because their preparation and investigation requires far more care and attention to details than real surfaces. Many investigators never obtained a clean surface to begin with, because of doubtful cleaning procedures:⁴ too high pressures during argon bombardment, gas burst during cleaving operation or formation of a p-type skin through boron diffusion from the glass walls. Other obtained a clean surface, but later may have contaminated it by contact with a dielectric material during field effect measurements.^{5, 6, 7}

To obtain some reliable information it was therefore thought worthwhile to employ a technique that has proved efficient on real surfaces and adapt it to clean ones, with special emphasis on perfect cleaning procedures. The technique chosen was that of combined surface recombination and conductivity measurements, one of the most sensitive methods for studying surfaces. It employs the field effect and would therefore be less effective on clean surfaces because of their strong p-type barrier, but it would be sufficient for determination of the field effect mobility. Measurements were performed on (111) and (100) faces of germanium and the results are reported here.

II. EXPERIMENTAL METHOD

1. Technique of Electrical Measurements

Simultaneous measurements of filament lifetime and conductivity were performed with a Many bridge.⁸ This method requires one of the sample's contacts to be slightly injecting and the other to be ohmic, for this purpose soldered contacts are usually used. No soldered contacts could be used here, because of their high vapor pressure at annealing temperatures, but it was found that gold plating the sample's edges resulted in slightly injecting and noise free contacts which withstood well the repeated heat treatments. The diffusion of gold into germanium at annealing temperatures (550°C) is negligible.

As a detector for the Many bridge the Tetronix Type 502, Double Beam Oscilloscope was used, one beam for conductivity and the other for lifetime measurements. Changes in the sample's resistance of one part in 10,000 could be easily detected. The accuracy of the lifetime measurements depended on the injecting properties and varied between 2 percent and 15 percent. dc voltages up to 1000 volts were used for the field effect; the absence of slow states at pressures at 10^{-7} and lower made ac voltages and phase shift arrangements⁸ unnecessary.

2. Crystal Mount and Field Plate Arrangement

The crystal mount and field plate arrangement are schematically illustrated in Fig. 1. The edges of the sample were pressed against two L-shaped graphite contacts G, one of them spring loaded. A precision ground quartz plate P was inserted between the sample and the base quartz plate A, so that the upper face of the sample was absolutely flush with the horizontal faces F of the graphite contacts. The field plate F_p , free to move in all directions, could be lowered until the 100 micron thick mica spacers M rested firmly on the graphite faces F. In this manner a strong, homogenous

electric field was obtained and the danger of contaminating the cleaned surface with a dielectric spacer was avoided. During ion or electron bombardments the field plate was retracted into a side tube, to prevent any sputtering onto the crystal face..

Figure 2 illustrate the main features of the experimental tube. The electron gun for ion bombardment etc. was at about 10 cm's distance from the field plate, so that after each cleaning operation the crystal had to be moved away from the electron gun and under the field plate. To accomplish this the sample holder was mounted on a carriage, which consisted of a nickel base B and two end plates H. The carriage could slide on the two tungsten roads R, which passed through slots in the end plates H. The sliding movement was magnetically operated, with the help of the nickel projections N which almost touched the inner wall of the glass tube. The tungsten rods R were held in position by a frame structure, consisting of two rails A_1 and A_2 and end rings D. The upper rail A_1 had two large slots, one for the electron gun and the other, not shown in Fig. 2, for the field plate. The metal tongues L pressed against the inner wall of the glass tube and the entire frame could be centered and positioned by adjusting screws, not shown in the figure. The two end rings D on each side of the frame also supported short glass tubes, through which passed the electrical connections (tungsten coils) to the graphite contacts. Not shown in Fig. 2 are quartz plates which covered the vertical faces of the contacts and prevented graphite from sputtering onto the crystal face, and mica spacers which insulated the contacts from the end plates H.

Figure 3 is an illustration of the field plate. The plate itself F_p was made from an H-shaped nickel block, the lower part precision machined to ensure absolute flatness. The nickel block was attached to a bar B (of square cross section) by two screws S, resting on the plate P. In this manner the nickel block had small freedom of movement in every direction and could easily "find its position" when lowered onto the graphite contacts. The frame, which held the bar B in position inside the vertical side tube, utilized a "clock construction." In the lowered position the nickel slug A' (for the

magnetic control) rested on the set screw R. To remove the field pole from the crystal mount, A was lifted and rotated until it rested on the set screw C. The two mica spacers M were attached to the field plate by two tungsten hooks.

During the first field effect measurements it was found that the field plate was very often "shortened" by small graphite or metal particles on the contacts. The thickness of the mica spacers was therefore increased from 40 to 100 microns and this prevented the occurrence of "shorts" in most cases. The capacity of the sample-field plate capacitor was 9 micro-microfarad.

3. Vacuum System

The ultrahigh vacuum system is illustrated in a block diagram, Fig. 4. The main system and the gas handling system were pumped by a fore pump and a single stage mercury diffusion pump to about 5×10^{-7} torr. The ultrahigh vacuum part of the system could be baked out at 280°C , this is the part above the dashed line in Fig. 4. It contained an omegatron mass-spectrometer of the type described by E. J. Zdanuk, et al.⁹, a "Varian Type V-11403" Vac ion pump (pumping speed: 5 l/sec), an "N.R.C. Model 552" Redhead magnetron gauge, a "Westinghouse WL5966" B-A ion gauge, and a "Wolsky, Type 3" molybdenum getter. The lowest pressures ($\sim 7 \times 10^{-10}$ torr) were obtained immediately after bakeout; after the bombardment and annealing processes it increased to about 8×10^{-9} to 2×10^{-8} torr. Residual gas scans were carried out after each operation as a routine procedure. During the adsorption runs a steady flow of oxygen was passed through the system at 2 l/sec and a pressure of about 5×10^{-6} torr was maintained and measured with the help of the Redhead magnetron gauge, which does not cause any CO_2 and CO conversion.¹⁰

The complete ultrahigh vacuum system was mounted on a mobile frame, constructed from ACME slotted angle steel pieces and topped by a

one inch thick transite plate (Fig. 5). The bakeout oven was suspended above it, so that after disconnecting the water hoses (to the mercury diffusion pump) the frame could be wheeled out from under the oven and be replaced by a similar ultrahigh vacuum system, on which other investigations were being performed.

4. Crystal Preparation and Surface Cleaning

All samples were cut from a 15 ohm-cm n-type single crystal obtained from "Semimetals, Inc." From this crystal the first slices were cut parallel to the 111 face (this was the direction in which the crystal was grown), it was then re-oriented by Laue X-ray back reflections, so that slices could be cut parallel to the 100 face. From these slices 0.4 cm wide rectangular strips were cut and ground down to a thickness of 0.05 cm. Resistivity scans were then performed to test if the doping was homogenous throughout the length of the strip and 2 cm long samples were cut off each strip accordingly. The edges of each sample were then gold plated. To ensure that only those parts of the crystal remained gold plated that actually touched the L-shaped graphite contacts (Fig. 1), the sample was ground down to a thickness of 0.45 cm and width of 0.39 cm. The final shape of the sample, prior to etching, was that of a parallelepiped with dimensions $2 \times 0.39 \times 0.045$ cm. The gold-plated edges were masked and the sample etched in CP4-A for one minute at 35°C, it was then stored in room air for a few days. The reason for this etching and storage in room air was, because this is one of the standard treatments for real surfaces and some samples were measured under ordinary vacuum conditions, to investigate their surface state parameters prior to ion and electron bombardment.

The cleaning procedure closely followed the ion-bombardment technique of Madden and Farnsworth.¹¹ The sample was argon bombarded for 40 minutes at a pressure of $(3-8) \times 10^{-3}$ torr using a controlled discharge produced by electron beams of 60-80 eV. The current density was 200-800 micro amps per cm² and the bombarding voltages were 500-800 v. The argon

was pumped out and the crystal annealed, by electron bombardment, to about 550°C for 15 hours. By slowly reducing the high voltage the sample was cooled down to room temperature in about five hours. During the ion bombardment the metal frame of the experimental tube (Fig. 2) was connected to the accelerating grid of the electron gun, during electron bombardment the frame was grounded. The annealing temperature of the sample was obtained by calibrating the bombarding electron current against a thermocouple attached to the crystal. The thermocouple wires were removed after the calibration curve had been obtained. To heat the crystal to 550°C about 15 watts were required (2000 volts, 7-8 mA), but a substantial part of this power was wasted on the graphite contacts.

The mica spacers (Figs. 1 and 3) insulating the graphite contacts from the field plate were originally clamped to these contacts. However, it was noticed that under electron bombardment the mica would start to glow brightly at certain spots and burn away at the edges, this would cause the pressure to rise from 10^{-7} to 10^{-5} torr. The mica, in addition to strong outgassing under electron bombardment, had another detrimental property: for bombarding voltages greater than 1000 volt its secondary electron emission coefficient seemed to be greater than unity. It therefore started to focus the electrons on itself and away from the crystal, which is very undesirable redistribution of electrons. For this reason the mica spacers were attached to the field plate, and this increased the crystal's temperature considerably (for the same electron current) and decreased the gas pressure during electron bombardment by two orders of magnitude.

III. EXPERIMENTAL RESULTS*

1. Interpretation of Data

The measured quantities were filament lifetime τ_f and filament resistance R_f , these had to be converted into surface recombination velocity s and surface conductivity $\Delta\sigma$. In calculating the values of s and $\Delta\sigma$ corrections had to be applied, to take into account that only one of the two large sample surfaces was ion bombarded and therefore atomically clean. Values of $\Delta\sigma$ were corrected by a method similar to that used by Forman.⁵ Preliminary oxygen adsorption experiments were performed on samples which were subjected to electron bombardment only. From these measurements the influence of the surface not exposed to argon bombardment could be determined. As will be shown in paragraph 3 of this section, the unbombarded surface changed relatively little with oxygen adsorption and therefore acted like a parallel resistor of almost constant value.

The surface recombination velocity s was corrected by employing:¹²

$$1 \dots \frac{1}{\tau_f} = \frac{1}{\tau_b} + \frac{s_1}{B} + \frac{s_2}{B}$$

Where: τ_b, τ_f = bulk and filament lifetime, B = half the sample thickness and s_1, s_2 are the surface recombination velocities of the two large sample surfaces. Equation (1) applies only for small values of s , i. e., as long as $\eta = \text{tg } \eta$.¹² This condition was fulfilled in almost all cases. It should also be remembered that for the interpretation of our data the changes in s are far more important than their absolute values.

*Partial results have since been published in Appl. Phys. Letters 2, 143 (1963) and Bull. Am. Phys. Soc. Series II, 8, 296 (1963), another part was reported at the 23rd Annual Conference on Physical Electronics, MIT, Cambridge, Mass. on March 20, 1963.

2. (111) Surfaces

Altogether three samples of (111) orientation were investigated, each was subjected to four or five oxygen adsorption experiments. Very similar results were obtained on all three samples.

The surface recombination velocities of the first samples (Se 1/6/1) in room air was 190 cm/sec, at 10^{-4} torr s was 360 cm/sec, and after bakeout and at 1×10^{-8} torr it increased to 550 cm/sec. This progressive increase was also observed by Madden and Farnsworth,¹¹ and is due to the removal of water vapor from the sample.¹³ The recombination velocity for the clean surface varied between 730 cm/sec and 480 cm/sec, Madden¹¹ quotes a value of 460 cm/sec and J. T. Law and C. G. B. Garrett¹⁴ measured 600 cm/sec on their p-type sample. However, when oxygen was admitted to the system results were obtained which differed significantly from those reported earlier.^{11, 14} The results of two different oxygen adsorption runs are represented in Fig. 6, which illustrates the changes in s and $\Delta\sigma$ as a function of the product (pressure \times time). Changes in $\Delta\sigma$ are relative to an arbitrary zero before oxygen admission. All in all five adsorption experiments were performed on this first sample. For the first three runs the surface was cleaned by ion bombardment and annealing, but for the last two it was cleaned by annealing only. Figure 6 gives the results for the third and fourth adsorption run. It is clearly seen that in both cases the surface recombination velocity first decreased and then, after about 300×10^{-6} torr min, started to increase and reached a value greater than that for the clean surface. Exactly the same behavior was observed on all adsorptions. After five consecutive runs on the first sample four additional experiments were performed on a second sample (Se 1/5/3). Here again very similar results were obtained, s first decreased and then increased with oxygen adsorption. Following the third adsorption, the sample was heated to 130°C at 3×10^{-6} torr oxygen pressure for over 15 hours, but this additional treatment decreased s by only ten percent. The changes in $\Delta\sigma$ with oxygen adsorption reported here agree very well with those previously observed by Law and Garrett¹⁴ and Palmer et al.¹⁵

Decrease of s with oxygen adsorption has never been observed before and it was thought that insufficient annealing after ion bombardment may have been the reason. The third sample (Se 1/4/3) was therefore annealed at temperatures lower than 550°C , before being exposed to oxygen. Figure 7 illustrates the results of two consecutive adsorptions, differing only in their annealing temperatures. When this temperature was below 500°C , no change in s was observed and the initial increase of $\Delta\sigma$ was small, but after re-annealing at 550°C the usual changes in s and $\Delta\sigma$ were observed. During another adsorption performed after insufficient annealing no initial change in s was detected, but after 10^{-3} torr min the surface recombination started to increase. In other words, results similar to those published by Madden¹¹ and by Law¹⁴ could be obtained by decreasing the annealing temperature. It should, however, be mentioned that in most cases the injecting properties of the gold-plated contacts improved with increased temperature. The accuracy and sensitivity of the lifetime measurements performed after insufficient annealing were therefore noticeably inferior to those preceded by higher annealing temperatures. Moreover, Madden¹¹ measured surfaces parallel to the (100) direction and here his results are in good agreement with ours, as will be seen later.

The third sample, after completion of an oxygen adsorption run, was exposed to the atmosphere. Field effect measurements then showed that the minimum of $\Delta\sigma$ could be reached. It was therefore possible to measure $\Delta\sigma$ in absolute units and thereby determine the surface potential¹⁵ $u_s = q\phi_s/kT$ throughout the entire range, starting with the clean surface at 10^{-8} torr and terminating with the real surface at 760 torr. The results are shown in Fig. 8, which also illustrates the energy level diagram of the clean (111) surface. E_V = top of valence band, E_C = bottom of conduction band, E_F = Fermi level, the intrinsic level E_i is indicated by the dashed line. The pressure scale in Fig. 8 is only approximate. The surface potential of the clean surface was $u_s = -9.6$, after 14×10^{-6} torr min it reached -9.75 and from thereon decreased continuously with oxygen adsorption. At atmospheric pressure $u_s = -3$; the minimum of $\Delta\sigma$ extended from (-1) to (-3) . These results therefore indicate that the clean (111) surface is highly p-type, but not degenerate.

The field effect mobility of the clean surface of sample Se 1/5/3 was $80 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ and p-type, in excellent agreement with the values (50-150) $\text{cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ quoted by Palmer et al.¹⁷ After oxygen adsorption of 450×10^{-6} torr min the mobility was $88 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ and p-type, i. e., it had hardly changed. Handler¹⁸ and Forman⁵ also reported that the field effect mobility remained almost constant during the initial phases of oxygen adsorption. The mobility of sample Se 1/4/3 at 10^{-5} torr and before the cleaning process was $90 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ and n-type; after the system was baked out and the pressure decreased to 5×10^{-9} torr the sample's mobility reached $200 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ (n-type).

3. (100) Surfaces

Two samples of (100) orientation were investigated, the first (Se 1/100/3/2) was subjected to four oxygen adsorption runs, the second sample (Se 1/100/2/1) to three runs. Because of the poorer injecting qualities of the contacts only two out of the seven adsorption runs permitted accurate measurements of filament lifetime; surface conductivity measurements were not adversely affected by this. The results of one of the adsorption experiments which permitted accurate lifetime measurements ($\pm 5\%$) are represented in Fig. 9. Two differences between these results and those corresponding to the (111) surfaces (Fig. 6) are noticeable: a) $\Delta\sigma$ decreases continuously and does not exhibit the initial rise encountered on the (111) surfaces, b) s remains unchanged up to about 10^{-4} torr min and then increases continuously. The independence of surface recombination of oxygen pressure (up to 10^{-4} torr min) was confirmed in all seven experiments and is therefore well established. However, careful measurements at low oxygen pressures (10^{-7} torr) performed on the second sample most definitely showed the initial rise in $\Delta\sigma$ observed on all (111) surfaces. In this respect the results illustrated by Figs. 9 and 10 are not typical and probably due to a too fast increase in oxygen pressure.

After the fourth adsorption experiment sample Se 1/100/3/2 was exposed to the atmosphere, the minimum of $\Delta\sigma$ could then be reached and

the surface potential u_s was determined. The results are shown in Fig. 10, which also illustrates the energy level diagram of the clean (100) surface. The surface potential of the clean surface was $u_s = -12.1$; the surface was therefore p-type and degenerate. Forman⁵ also found that the (100) surface was more p-type than the (111) surface, but did not quote any values. The lifetime measurements were of very poor accuracy and all that can be said is, that s seemed to remain more or less constant ($\pm 30\%$) throughout the entire adsorption run.

Results obtained on sample Se 1/100/2/1 after it was heated to 550°C for 15 hours, without any previous argon bombardment indicated, that changes in $\Delta\sigma$ (relative to $\Delta\sigma = 0$ before heating) were smaller by one order of magnitude compared to argon bombarded surfaces. The initial increase, after 0.14×10^{-6} torr min, was $0.57 \mu\text{mho cm}^{-2}$ and the final decrease, after 2100×10^{-6} torr min, was $8.3 \mu\text{mho cm}^{-2}$. The changes in s , however, were of the same order of magnitude and the "unclean" (100) surface behaved quite similar to the clean (100) surface. Figure 9 illustrates the most extreme case of changes in s encountered on an argon bombarded and annealed surface; usually s remained quite constant even up to to 300×10^{-6} torr min. Farnsworth¹⁹ has conclusively demonstrated that heating alone (even up to just below the melting point) will not result in a clean surface; moreover, the surface may be covered by a p-type boron skin.²⁰

Values of field effect mobility measured on sample Se 1/100/3/2 were as follows:

At 5×10^{-9} torr, before argon bombardment:	$470 \text{ cm}^2 \text{v}^{-1} \text{sec}^{-1}$ (n-type)
After argon bombardment:	$35 \text{ cm}^2 \text{v}^{-1} \text{sec}^{-1}$ (n-type)
Clean surface	$165 \text{ cm}^2 \text{v}^{-1} \text{sec}^{-1}$ (p-type)
After oxygen adsorption at 10^{-5} torr oxygen pressure	$180 \text{ cm}^2 \text{v}^{-1} \text{sec}^{-1}$ (p-type)
After exposure to atmosphere	$140 \text{ cm}^2 \text{v}^{-1} \text{sec}^{-1}$ (p-type)

The extreme low value of the mobility after argon bombardment is remarkable, similar results were also obtained by Forman.⁵ After exposure to the atmosphere the surface conductivity was very near its minimum, which explains the low value of $140 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$.

4. Slow States Relaxation Effects

It was inevitably observed on all samples that the slow states relaxation effects (of s and $\Delta\sigma$) disappeared after the vacuum system had been baked out and a pressure of 5×10^{-9} torr obtained. The same observation has been reported by Palmer et al.¹⁵ and by others.²¹ To shed some additional light on this subject, the following sequel of experiments was performed. Sample Se 1/4/3 was etched in CP-4A and stored in room air for a few days. It was then introduced into an ordinary vacuum system and the relaxation effects of s and $\Delta\sigma$ were measured at 2×10^{-5} torr. These effects were of exactly the same nature as those reported by Many et al.²² The sample was removed and introduced into the ultrahigh vacuum system, where it was subjected to ion bombardment, electron bombardment, and oxygen adsorption experiments. After the completion of the fifth adsorption run the sample was exposed to the atmosphere and tested for relaxation effects. At atmospheric pressure these effects were present. When evacuated to 2×10^{-5} torr no effects whatsoever could be observed, though fields of 1×10^6 volts/cm were applied for five minutes and resistance changes of 0.02 percent could have been detected. This proves that the relaxation effects observed under ordinary vacuum conditions are not caused by any ad- or desorption of ions from the surrounding ambient, as was assumed by Law²³ and by Lyashenko et al.²⁴ In fact, the relaxations are not related at all to the ambient but inherent in the oxide structure that covers the germanium surface. The slow states are probably very closely connected with water molecules in the oxide structure,²⁵ because the germanium oxide covering the clean surface was formed with no traces of water vapor present and indeed did not show any relaxation phenomena.

5. Residual Gas Analysis

Table I summarizes the main features of residual gas scans during various stages of the research. The results are quoted in percentage of total pressure and therefore indicate directly the composition of the residual gas. The following features are noteworthy: 1) The percentage of oxygen (mass-number 32 and 16) at pressures below 8×10^{-8} never exceeded ten percent. 2) Argon, once admitted to the system, is persistently present and its percentage increases the lower the total pressure. It is also mainly responsible for the pressure rise during electron bombardment and does not disappear, even after prolonged heating. Argon ions, even at such low energies as 600-800 ev, seem to penetrate quite deeply into the crystal²⁶ and into the graphite contacts. 3) The very small oxygen conversion effect¹⁰ of the well-decarbonized omegatron filament should be noted (Scan No. 5). 4) The efficiency of the getter in pumping oxygen is well illustrated by comparing scans No. 6 and No. 7.

These results are similar to those reported by Wolsky and Zdanuk.²⁷ Three massnumbers higher than 44 were consistently encountered: 200, 110, and 70. Massnumber 200 was most probably due to Hg^+ and 110 might have been Hg^{++} , but the origin of massnumber 70 remained a mystery.* The resolution of the omegatron for these high massnumbers is poor and for this reason no satisfactory evidence for either GeO^+ or GeO_2 could be found.

*The obvious suggestion would be Ge^+ (massnumber 72.6) but the following two facts almost rule it out: 1) The distance between the crystal and the omegatron was about 40 cm and no traces of Ge could possibly reach the omegatron. 2) The massnumber 70 peak was not increased when the sample was heated by electron bombardment.

TABLE I - Section 2

No.	Conditions	Ions	N ₂ ⁺										CH ₄ ⁺ (CO) ⁺⁺				Total Pressure (torr)
			Massnumber (%)	CO ₂ ⁺ (%)	A ⁺ (%)	O ₂ ⁺ (%)	O ₂ ⁺ (%)	CO ⁺ (%)	CO ₂ ⁺⁺ (%)	A ⁺⁺ (%)	H ₂ O ⁺ (%)	OH ⁺ (%)	O ⁺ (%)	N ⁺ (%)	C ⁺ (%)		
1	After System Was Baked Out		>44	44	40	32		28	22	20	18	17	16	14	12	8×10 ⁻⁸	
2	Electron Gun Outgassing		0.7	8.8	1.7		76				4.8	1.5	1.7	0.7	1.2	1×10 ⁻⁶	
3	After Argon Bombardment		3	24	19		34	1	12	4.6	4.6	1.7		---	---	3×10 ⁻⁸	
4	Crystal Heated by Electron Bombardment		10	7.6	53		17	2.3	6	2.3	2.3	1.5		---	---	2×10 ⁻⁷	
5	During Oxygen Adsorption		---	7.4	3	76.5	3				10					1×10 ⁻⁵	
6	After Oxygen Adsorption			26	11.3	20	25		0.4	9	3	4	0.8			2×10 ⁻⁷	
7	After Flashing Getter		1.3	25	22	7	15		1.3	17	7.6	3	1			5×10 ⁻⁸	

IV. CONCLUSIONS AND DISCUSSION

The results reported here indicate that the clean (111) germanium surface is strongly p-type, but not degenerate and the valence band is at a distance of about $q\phi = 3kT$ below the Fermi level. The surface recombination is not space charge limited and is noticeably affected by oxygen. The changes in $\Delta\sigma$ and s after admitting oxygen to the clean surface (Figs. 6 and 8) can most simply be explained²⁸ by assuming the surface to become even more p-type during the initial phases of oxygen adsorption, up to about a monolayer or so, followed by a continuous decrease of the surface potential toward the "flat band" configuration. This would also account for the rise in work function observed by Dillon and Farnsworth² on (111) and (100) surfaces.

In calculating the values of u_s from the experimental results of $\Delta\sigma$ no "Schrieffer corrections"²⁹ were applied and the bulk values of the mobilities were used. Lacking reliable experimental confirmation of Schrieffer's corrections, this is the best one can do. This uncertainty for the hole mobility at a highly p-type surface will cause some error in the value $u_s = -9.6$ of the surface potential, but it can hardly be greater than (± 1), because of the steepness of the $\Delta\sigma(u_s)$ curve in this region. Palmer et al³⁰ reported a value of $0.33 \text{ eV} = -12.5 kT$ for their cleaved surface (111) surface (measured on a pnp transistorlike structure of 7 ohm cm resistivity) i. e., the Fermi level at the surface was near the edge of the valence band. This indicates a p-type degenerate surface; however, recent results obtained at the Bell Telephone Laboratories³¹ showed that the clean germanium surface was not degenerate.

The clean (100) surface is p-type degenerate and the valence band touches the Fermi level. Madden's¹¹ previous findings were confirmed and the surface recombination is almost unaffected by oxygen adsorption. This is a most surprising result. During the initial stages of oxygen adsorption one may assume⁴ that s does not change because it is space charge limited, i. e., the strong p-type barrier prevents the electrons from reaching the surface. But this cannot explain why s remains constant even beyond $u_s = -9.6$,

Because we now know that s does change in this region. One must therefore assume that the oxygen does not only change u_s but affects the surface state parameters themselves and in such a way, that s is kept constant, e. g., by increasing the density and the energy of the states. This statement is probably true, but it is of very general natures and helps little. One might also suggest that the energy of the states on the slightly oxidized surface is extremely high, so that the plateau of the $s(u_s)$ curve³² extends from about $u_s = -9$ to $u_s = -3$. This is not impossible, but extremely unlikely and is not supported by any evidence from our relatively extensive knowledge about fast states on real states.

The remarks made previously on the possible error in the value of u_s for the clean (111) surface also apply to the value of $u_s = -12.1$ for the (100) surface. The values of $\Delta\sigma$ were calculated with the tables³³ and the bulk value of the mobility was used throughout. Our value of u_s should be taken as a lower limit, i. e., our results indicated that the surface potential of the (100) surface was at least $u_s = -12.1$. It is very unfortunate that the electron affinity for the (100) surface is not known, otherwise one may have obtained a good estimate on the decrease of hole mobility for a degenerate surface by comparing Dillon's² results on work function with ours on surface conductivity.

V. ACKNOWLEDGMENTS

The author would like to express his sincerest thanks to Dr. S. P. Wolsky, Dr. E. J. Zdanuk, and Dr. D. Shooter for their help in designing and operating the ultrahigh vacuum system. Prof. H. E. Farnsworth's and Prof. J. A. Dillon's assistance during the design of the experimental tube was very much appreciated. I am also indebted to J. Silva for supervising the construction of the tube, to L. Rubin for his assistance with the electronic equipment, and to W. Gowell and J. Gage for all the glass work. R. Leighton's technical assistance was invaluable.

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FIGURE CAPTIONS

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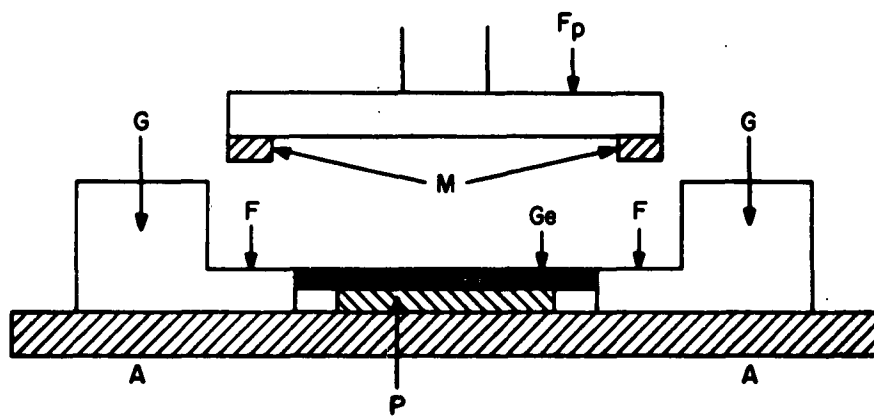


FIGURE 1

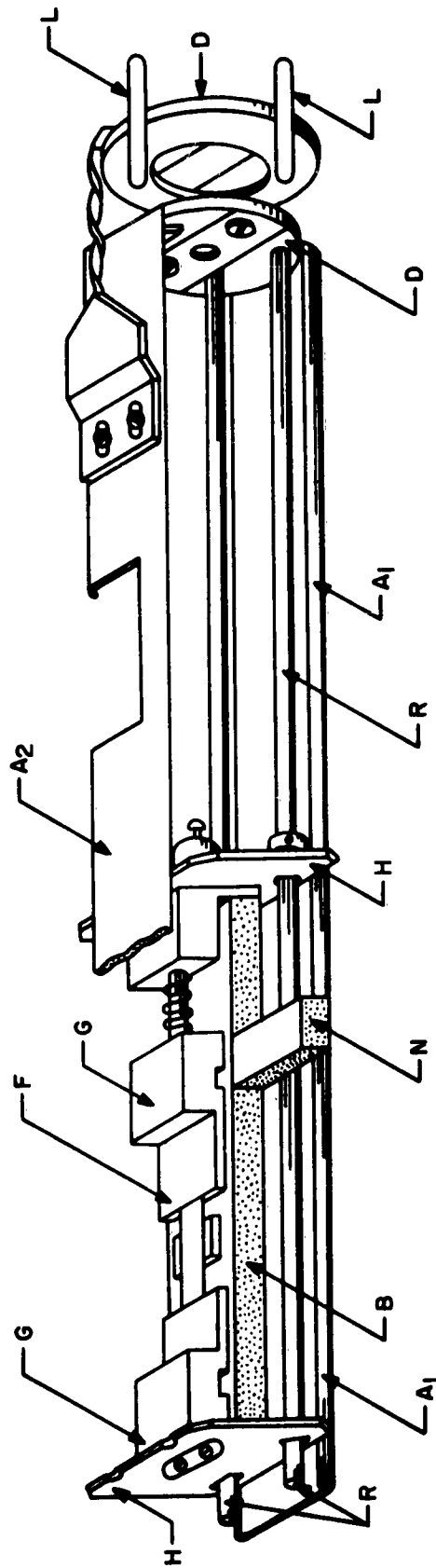


FIGURE 2

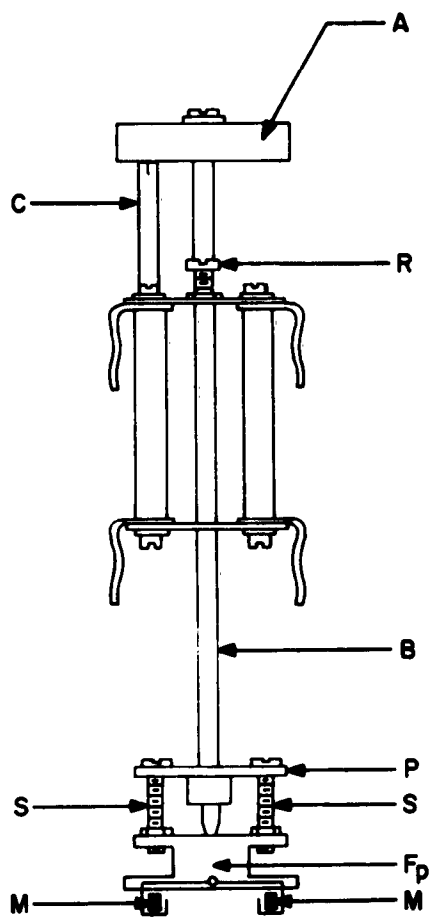


FIGURE 3

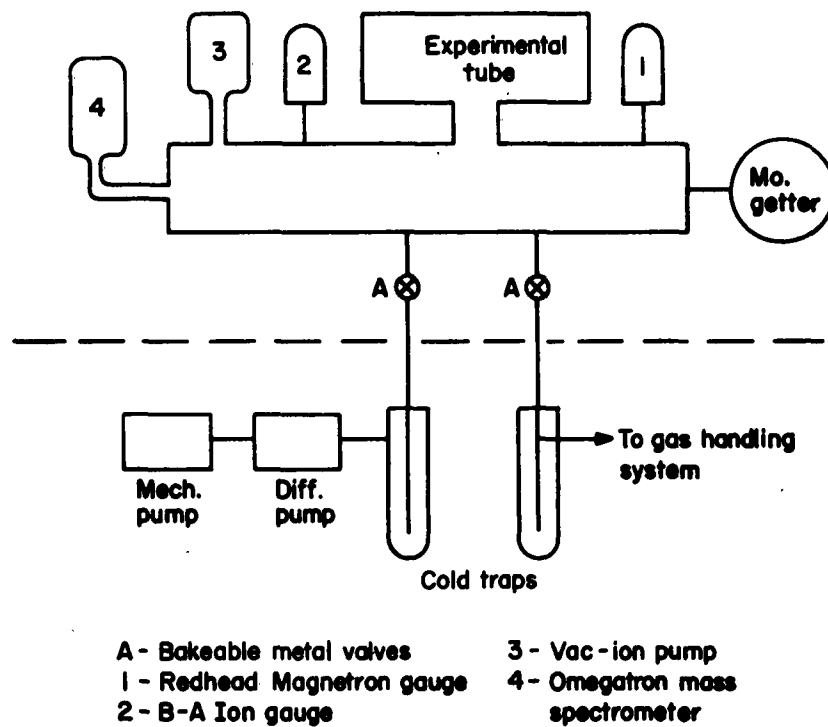


FIGURE 4

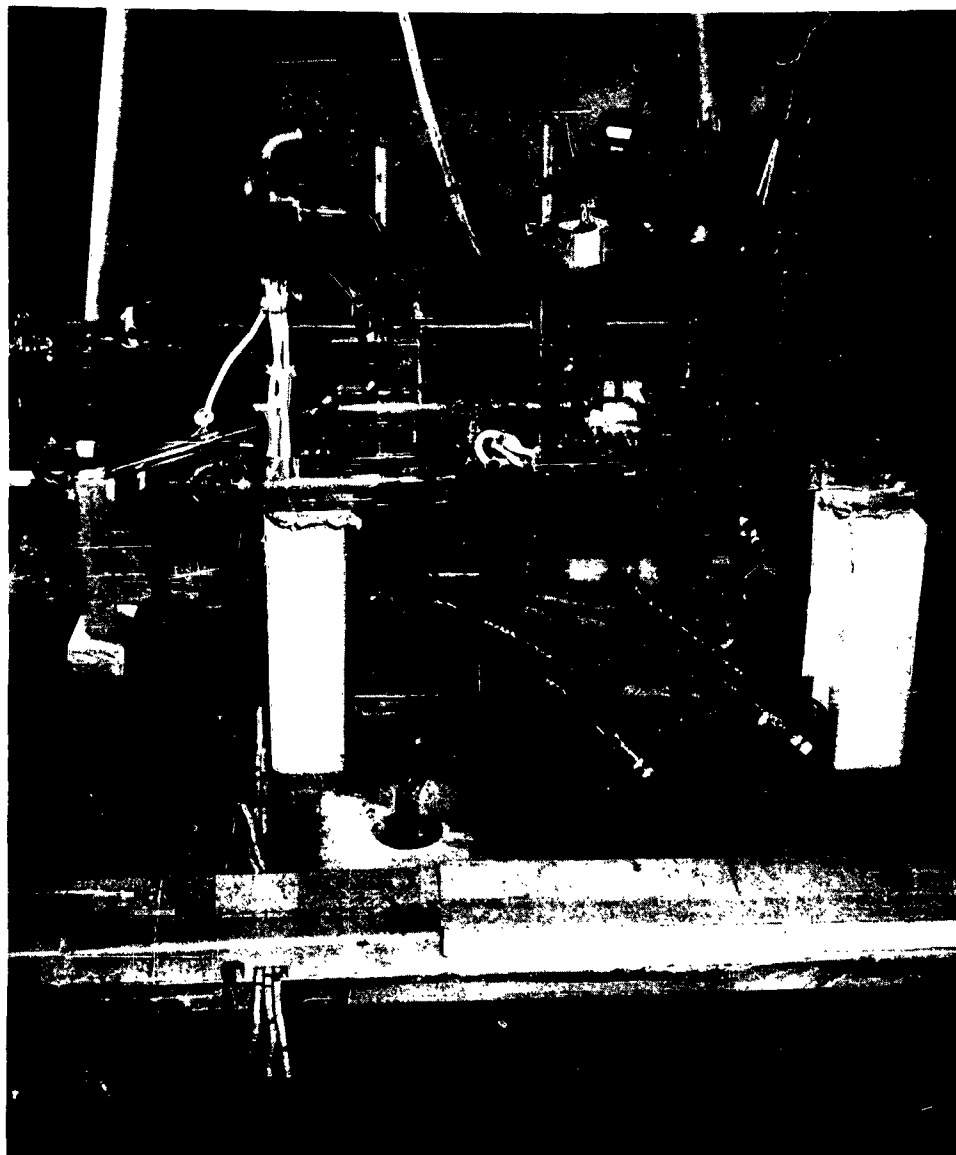


FIGURE 5

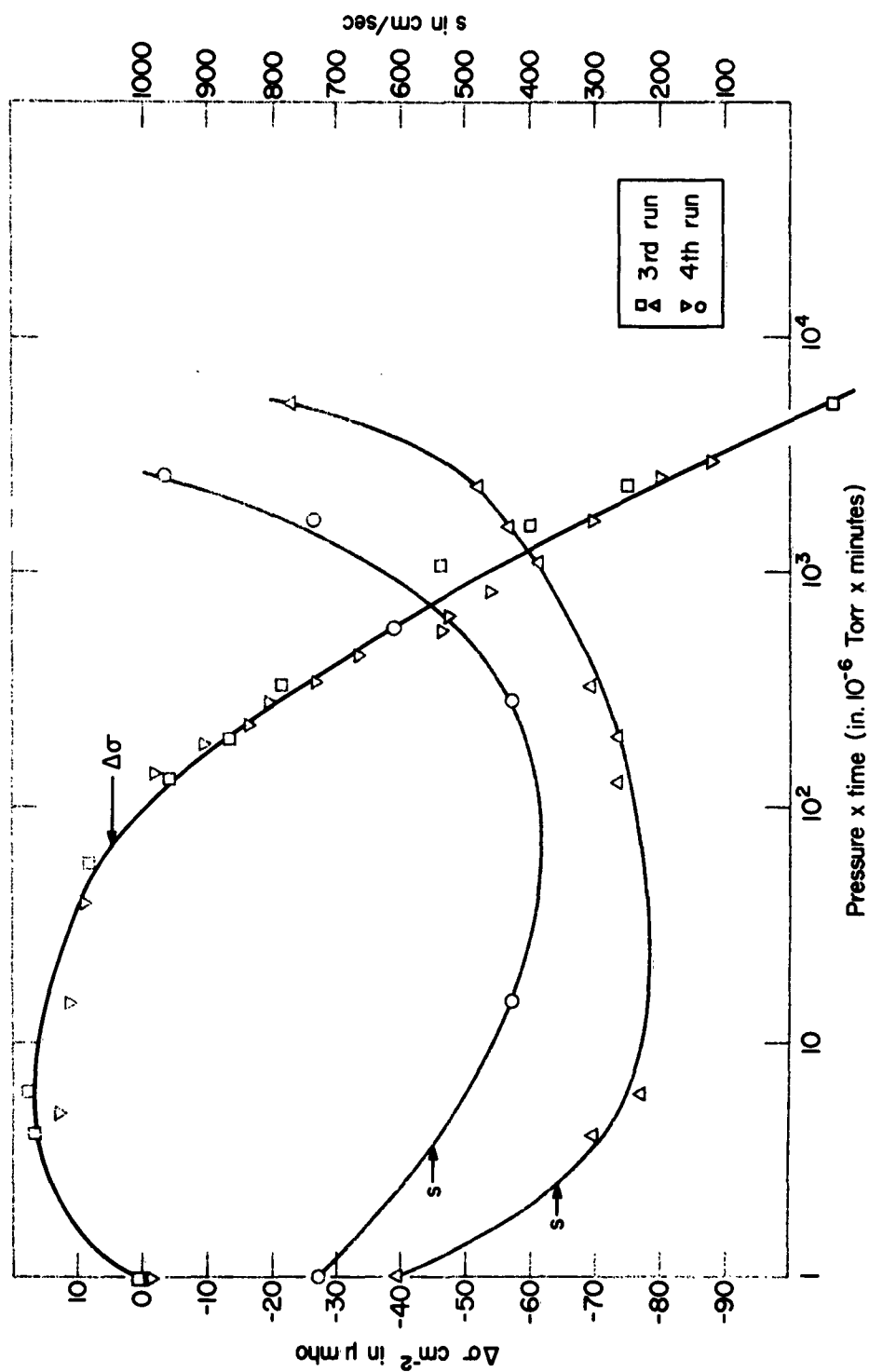


FIGURE 6

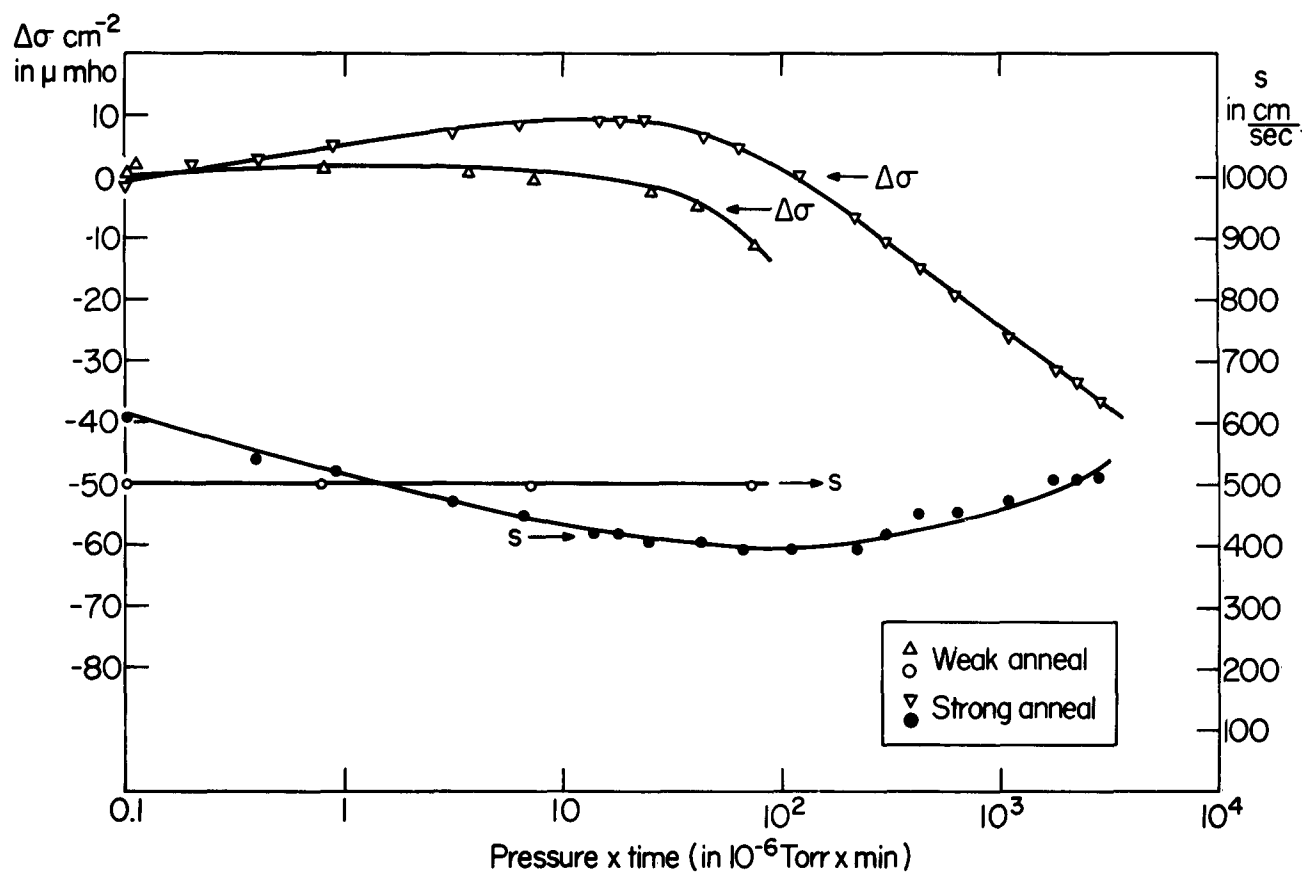


FIGURE 7

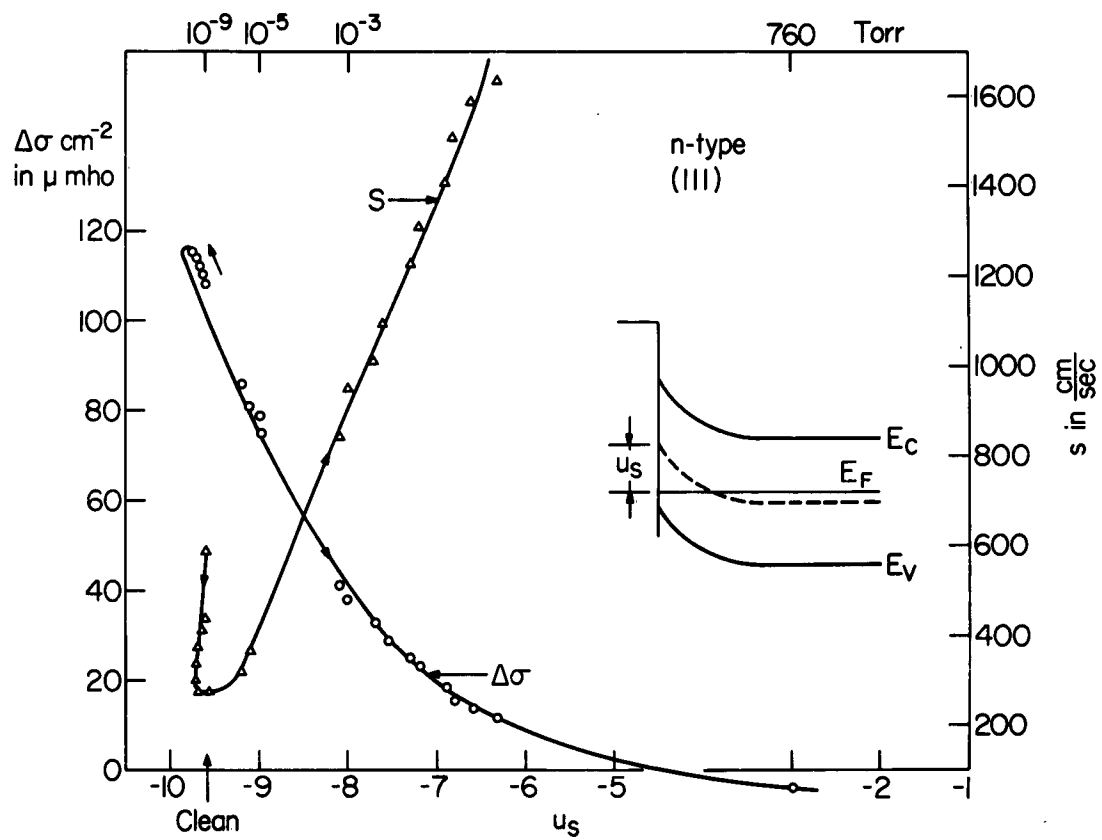


FIGURE 8

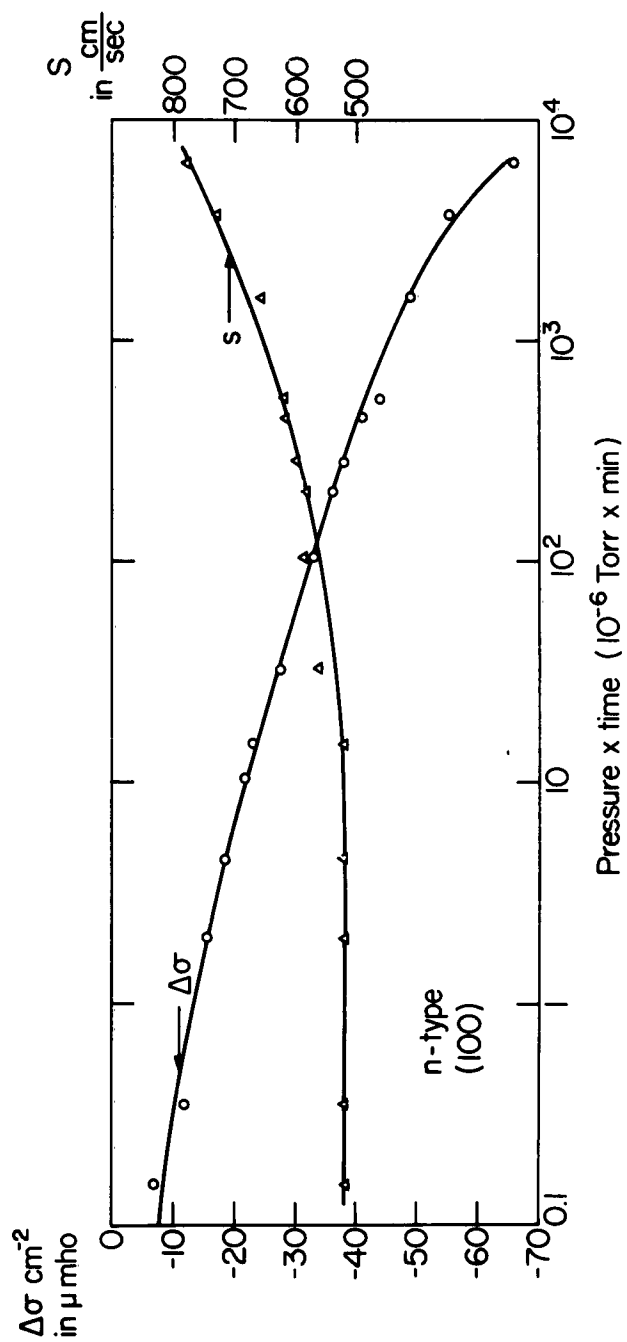


FIGURE 9

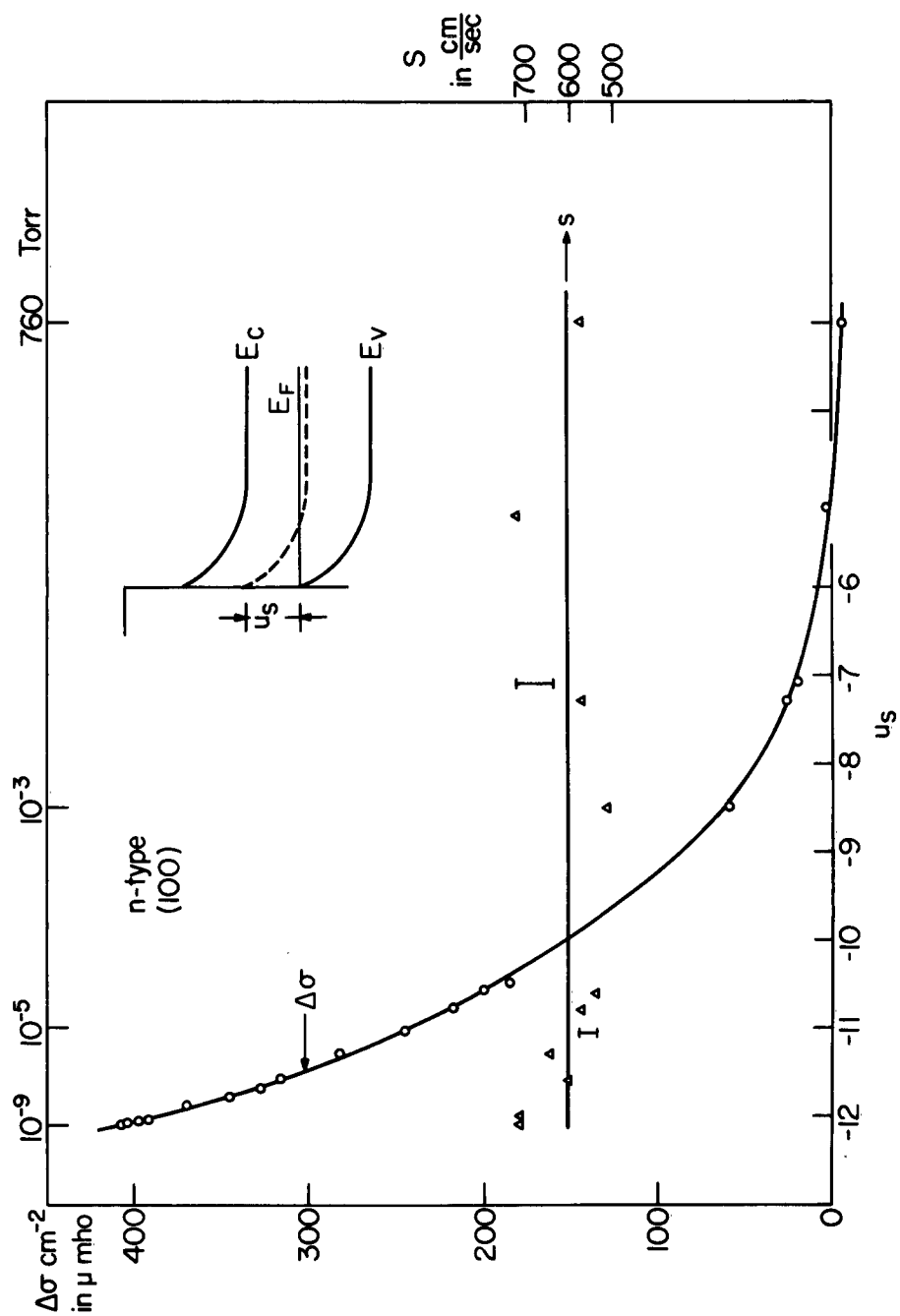


FIGURE 10

<p>Raytheon Company, Waltham, Mass. INVESTIGATION OF EFFECTS OF ION-INDUCED DEFECTS ON SURFACE REACTIONS, by Y. Margoninski and D. Shooter. AFCRL-63-162. Final Report, Contract No. AF 19(604)-8004, 20 January 1961 - 19 January 1963 (S-545). 46 pp.</p> <p>This Final Report is written in three separate series, corresponding to the three major projects specified in the work statement of the contract:</p> <p>Project A: Sputtering and Adsorption Properties of the (111) Faces of Gallium Antimonide</p> <p>Project B: A Survey of the Electrical Measurements Suited for Studying the Effects of Adsorbed Species on Surface Phenomena</p> <p>Project C: Simultaneous Measurements of Filament Lifetime and Surface Conductivity on Clean and Oxidized Germanium Surfaces.</p>	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> 1. Solid State Chemistry 2. Gallium Compounds 3. Germanium Compounds <ol style="list-style-type: none"> I. Margoninski, Y. II. Shooter, D. <p>UNCLASSIFIED</p>
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